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Publisher's version / Version de l'éditeur:
https://doi.org/10.1080/10916466.2010.495959
Petroleum Science and Technology, 30, 9, pp. 915-923, 2012-03-19

Petroleum Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lpet20

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Available online: 19 Mar 2012

To cite this article: P. H. J. Mercier, S. Ng, K. Moran, B. D. Sparks, D. Kingston, L. S. Kotlyar, J. Kung, J. Woods, B. Patarachao & T. McCracken (2012): Colloidal Clay Gelation: Relevance to Current Oil Sands Operations, Petroleum Science and Technology, 30:9, 915-923

To link to this article: http://dx.doi.org/10.1080/10916466.2010.495959

Petroleum Science and Technology, 30:915–923, 2012

ISSN: 1091-6466 print/1532-2459 online
DOI: 10.1080/10916466.2010.495959

Colloidal Clay Gelation: Relevance to Current Oil Sands Operations

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Abstract *Ultrafines are predominantly delaminated colloidal clays with dimensions <0.3 μm that exist naturally in oil sands and are released during conditioning of surface-mined ores. Critical concentrations of these ultrafines and the cations present in process water are capable of forming flocculated structures with a very high water holding capacity. During primary separation of bitumen these ultrafines are detrimental to recovery as a result of increased slurry viscosity as well as through slime coating of released bitumen. Disposition into tailings ponds eventually produces mature fine tailings (MFT) as a result of thixotropic gel formation that entraps coarser solids. The ultrafines concentration of ∼3 wt% observed in MFT coincides with the critical gelation concentration determined for suspensions of ultrafines in salt solutions with cationic concentrations representative of that in pond water. This observation accounts for 100% of the water holding capacity of MFT and also explains why virtually no water is released once an MFT gel state has been formed. Here, we review earlier research in this area and identify the harmful effects of ultrafines in some current problematic ores.*

Keywords bitumen recovery, gelation, oil sands, slime coatings, sludging, tailings, ultrafines

1. Introduction

Colloidal material occurring naturally in oil sands ores comprises phyllosilicate clays only a few layers thick (1–8 nm) with major lateral dimensions <0.3 μm (Kotlyar et al., 1993; Kotlyar et al., 1995). During conditioning in conventional water-based separation processes, the dispersion of this ultrafine material into the oil sands slurry depends on ore type as well as the mechanical and chemical dispersion energy used in the extraction process (Kotlyar et al., 1985). It has been demonstrated (Kotlyar et al., 1996) that in the presence of a sufficient concentration of cations only a small amount of ultrafines (∼3 wt%) is required to form a thixotropic gel with a very high water holding capacity. For ultrafines concentrations up to this critical gelation concentration slurry viscosity appears

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to increase progressively, thereby inhibiting settling of coarser solids and separation of bitumen droplets from the middlings zone of a gravity separation vessel (GSV). In extreme cases the formation of a dense sludge in the GSV requires operational shutdown. Organic matter adsorbed on these colloidal solids may produce biwettable characteristics that results in strong attraction to bitumen-water interfaces. Slime coatings of extremely small particles are capable of stabilizing bitumen as smaller, more difficult to float droplets (Kasongo et al., 2000; Levine et al., 2000).

When the slurried waste solids from bitumen separation processes are disposed into tailings ponds the coarsest solids separate rapidly to form beaches. Finer suspended material is carried out into the pond, slowly releasing water as it settles to produce mature fine tailings (MFT). The MFT always contains close to 3 wt% of ultrafines, an amount sufficient to produce a gel with enough internal volume to incorporate all of the water present in mature tailings (Kotlyar et al., 1992). Coarser solids carried into the pond become entrapped within the gel structure to produce the final solids concentration of about 30 wt% observed in MFT.

In this article we summarize previous research on the role of ultrafines in bitumen separation from oil sands and MFT formation.

2. Ultrafines Properties

2.1. *Nature of Ultrafines*

Techniques have been developed for the quantitative separation of ultrafines from both oil sands ores and MFT. These methods involve chemical dispersion of the solids with mild agitation (Kotlyar et al., 1985) followed by sequential application of increasing centrifugal force to separate the solids into size fractions based on differential sedimentation. For separating ultrafines from MFT (Kotlyar et al., 1992), repeated washing and centrifugation steps allow the original salty water to be replaced by deionized water to produce completely dispersed systems (colloidal sols); the process is completely reversible.

Transmission electron microscopy of separated ultrafines material (<0.3 μm), see Figure 1, shows broken, hexagonal clay particles with lateral dimensions of 60–270 nm, 1–8 nm thickness (Kotlyar et al., 1998). Particle thickness increased with lateral dimension. All ultrafines material is associated to some degree with organic material (Kotlyar et al., 1992). When the amount of organic is low the solids are predominantly associated with the aqueous phase, intermediate amounts of surface organics produce biwettable characteristics where solids preferentially collect at interfaces, ultimately the highest organic levels result in a fraction that remains exclusively with the bitumen phase (Kotlyar et al., 1988). A wettability study (Darcovich et al., 1989) confirmed that the aqueous ultrafines were indeed more polar and less hydrophobic than the ultrafines associated with bitumen. Surface analysis (Bensebaa et al., 2000) indicated patchy surface coverage by both humic and asphaltic components.

An X-ray diffraction (XRD) methodology was recently developed to analyze clay minerals in oil sands (Mercier et al., 2008a; Mercier et al., 2008b). This XRD technique has produced similar results to existing ultrafines measuring techniques by estimating the fraction of phyllosilicate mineral crystallites with 1–3 composite layers thickness in clays (<3 μm solids) separated from oil sands. Illite-to-kaolinite mass ratios were shown to increase as particle size decreased. The XRD powder pattern of the smallest size fraction of a waste unit sample (i.e., overburden barren clay-size material) was demonstrated to correspond to delaminated illite rather than kaolinite. Application of the

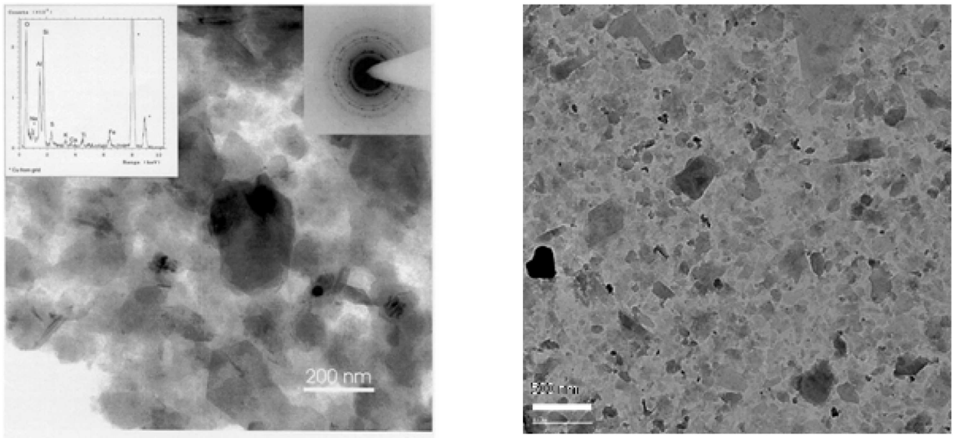

Figure 1. Typical transmission electron microscopy micrographs of ultrafines separated from Athabasca oil sands.

new XRD technique to 10 oil sands from current operations showed that the specific surface area of illite was significantly greater for four samples identified as problematic in batch-extraction unit (BEU) tests.

2.2. Flocculation and Gelation of Ultrafines

Settling tests allow evaluation of the size, density and settling rates of particle aggregates or flocs (Kotlyar et al., 1998). The lowest concentration at which a well-defined interface formed decreased with ultrafines particle size and increase in salt concentration. Such hindered settling occurs when flocs interact and no longer settle freely, see Figure 2. At

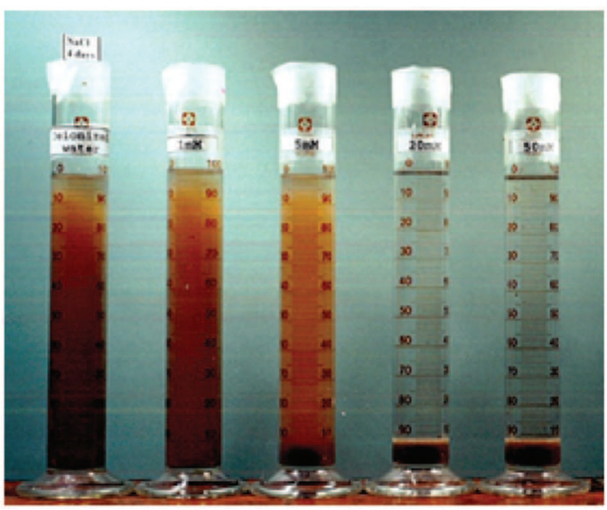

Figure 2. Effect of salt concentration on the settling behavior of dilute suspensions of ultrafines. From Kotlyar et al. (1996, Figure 3). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*. (color figure available online)

equilibrium, the settled volume fraction of the individual size components in the sediment ranged from 0.004 to 0.014 for the finest (60 nm) to coarsest sizes (270 nm). Different mixtures of ultrafines sizes yield final volume fractions between these values.

Photon correlation spectroscopy measurements to determine changes in floc diameter with time allow flocculation kinetics to be investigated (Kotlyar et al., 1996). Figure 3 presents results for a solids concentration (0.06 vol%) low enough to allow sufficient time to observe the kinetics. At low concentrations of salt (5 and 10 mM NaCl = 115 and 230 ppm Na^+) the repulsion between particles is still sufficient to inhibit sticking collisions (Weitz et al., 1991) and floc growth is slow; this corresponds to a reaction-limited regime. At a higher salt concentration (20 mM NaCl = 460 ppm Na^+), floc growth is initially reaction limited but much more rapid. At longer times floc growth slows owing to the increased time required for larger flocs to encounter each other; in this region reaction is diffusion limited. The settling tests summarized on Figure 4 show that rapid water release for recycle is favored by fast flocculation whereas slow floc growth produces higher sediment density.

A gelation index (GI) can be determined by NMR measurements (Ripmeester et al., 1993) on clay suspensions in the presence of different cations (Kotlyar et al., 1996). This approach allows the gelation process to be studied for concentrations of ultrafines and cations typically encountered in actual oil sands separations. The results in Figure 5 demonstrate that complete ultrafines gelation (i.e., a GI of 100%) requires sufficient time plus critical ultrafines and cation concentrations. In this regard total cation concentration is more important than cation valency. An equivalent monocation concentration can be estimated using the valency rule (Adam, 1956) that postulates an order of magnitude increased flocculation effect of divalent over monovalent cations. Depending on overall cation concentration, a space-filling gel network is produced in a matter of minutes by an ultrafines concentration of 1.2 vol% (~3 wt%). The same result is achieved over correspondingly longer time periods for lower concentrations of either ultrafines or cations. While complete gelation occurs almost instantaneously at 3 wt% ultrafines, significant effects are noted at a gel onset concentration (GOC)

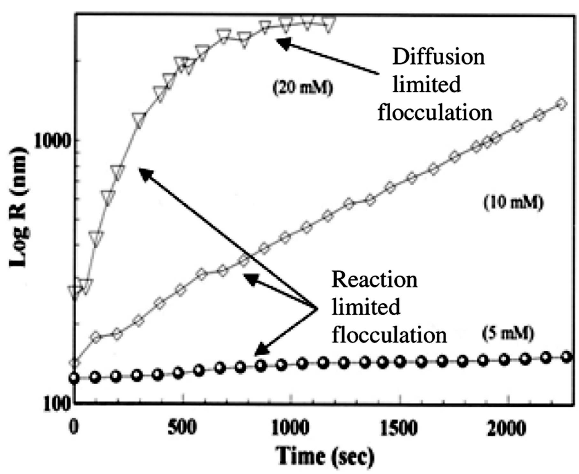

Figure 3. Cluster size (R) versus time in dilute suspensions of ultrafines for different salt concentrations. From Kotlyar et al. (1996, Figure 1). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

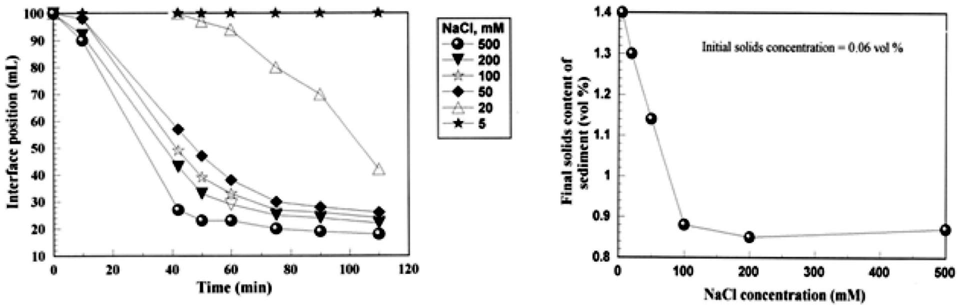

Figure 4. (Left) Time dependence of water release (mL) from dilute suspensions of ultrafines in salt solutions of different concentrations. (Right) Effect of salt concentration on solids content of sediments after six months settling of dilute suspensions of ultrafines in salt solution. From Kotlyar et al. (1996, Figures 2 and 4). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

as low as 1.0–1.4 wt% (O'Carroll, 2000). Flocculation, and ultimately gelation, of coarser clay fractions (2–3 μm) also occurs in the presence of cations but compared with ultrafines much higher solids concentrations (>10 wt%) are needed (Tu et al., 2005).

3. Application to Commercial Operation

In conventional, water-based oil sands extraction, primary separation of bitumen is essentially a gravity-based process. Once bitumen is liberated its separation into the froth depends on many factors, including: slurry viscosity (Schramm, 1985), relative density of bitumen to slurry (Shaw et al., 1996), droplet size (Ng et al., 2000), and aeration

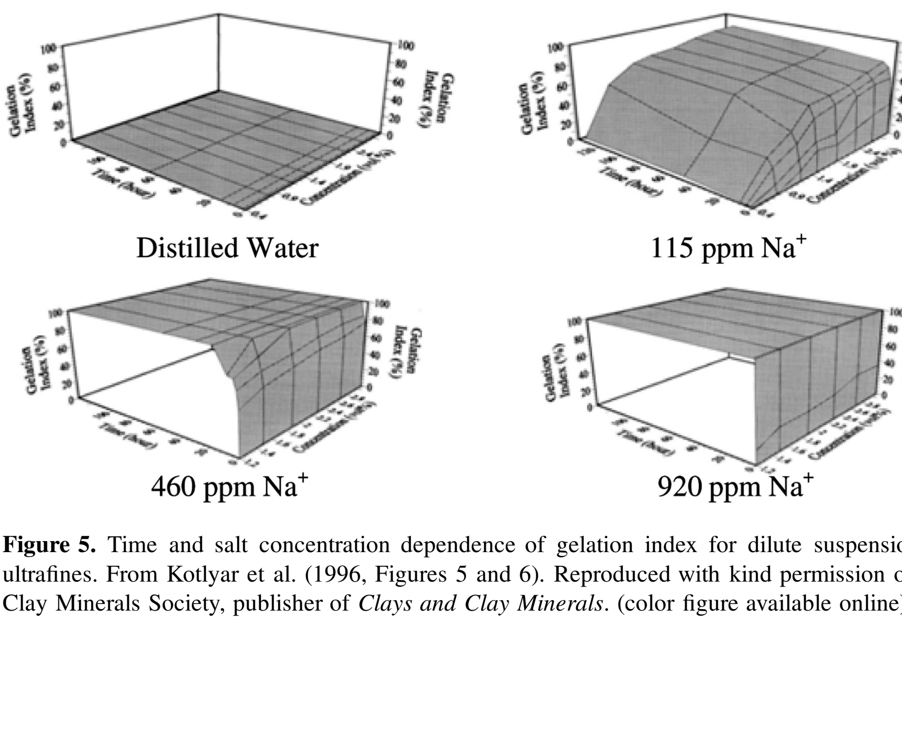

Figure 5. Time and salt concentration dependence of gelation index for dilute suspensions of ultrafines. From Kotlyar et al. (1996, Figures 5 and 6). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*. (color figure available online)

(Kasongo et al., 2000). Even if all other factors are favorable, high slurry viscosity may be a deciding factor because the free movement of oil droplets through the middlings into the froth will be hindered and perhaps prevented entirely.

In this regard, flocculation and gelation may be associated with reduced segregation of solids and bitumen in GSV middlings. Based on either fines or bitumen contents, the examples given in Figure 6 represent two ores that were not expected to exhibit poor bitumen recovery. However, the significant difference in segregation behavior is a reflection of very different processability in the two cases. Poor segregation, with concomitant low bitumen recovery, is associated with the oil sands containing ultrafines in excess of the GOC (1.8 cf. 1.4 wt%). By comparison, a low-value ultrafines content (0.5 wt%) in the other oil sands is linked to good bitumen recovery. Increasing the water to slurry ratio reduces the ultrafine concentration in the middlings and allows segregation of solids and bitumen while recovery proceeds normally in both cases. Similar effects can be achieved by blending ores with high and low ultrafines content. Flocculation in the middlings can also be reversed by use of dispersion agents, while sodium hydroxide falls into this category stronger agents such as silicates or phosphates may also be used.

As mentioned previously, a long-standing guideline for oil sands processability has been fines (<44 μm) or the related bitumen content (Cuddy, 2000). However, some ores do not fit this profile and the number appears to be increasing as new areas are opened for mining. An explanation for this phenomenon can be seen on Figure 7 where fines are plotted against the corresponding ultrafines contents; the dotted curves are the 95% confidence limits for the linear regression. It is apparent that there is a reasonable correlation between fines and ultrafines in most cases. However, in some instances there is a marked deviation as indicated by the noted anomalous oil sands.

The results on Figure 8 compares total solids with ultrafines present in the middlings zones of BEU and pilot tests. The pilot test involved an anomalous ore containing 2.9 wt% ultrafines, but only 13 wt% fines. During the test, solids content in the middlings progressively increased until it reached ~30 wt%; at this point process failure required a plant shutdown. Ultrafines content of the middlings was then about 2 wt%, well above the GOC. Usually, the amount of ultrafines released into the middlings is about 70%

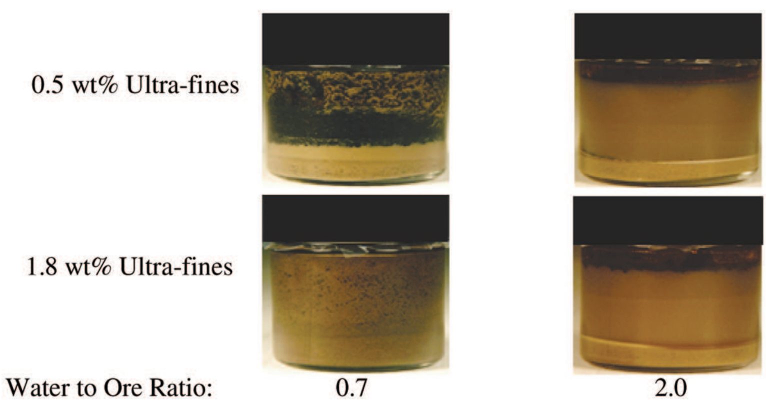

Figure 6. Oil sands with different ultrafines content at different process water to ore ratios. After O'Carroll (2000). (color figure available online)

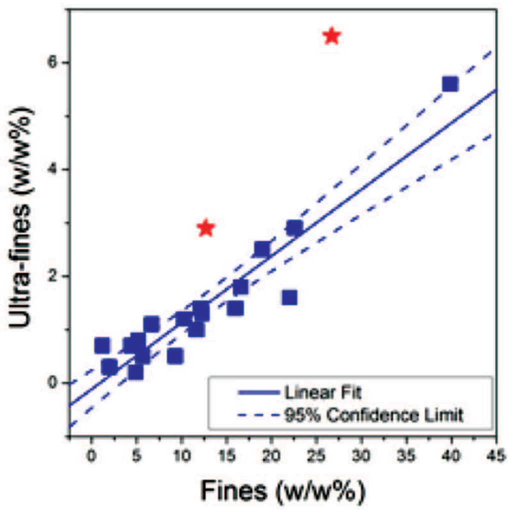

Figure 7. Ultrafines versus fines contents for a number of oil sands. Data from O'Carroll (2000). (color figure available online)

of that in the original ore (O'Carroll, 2000); this is in accord with the results from the anomalous ore in this case.

On average, the amount of ultrafines in tailings from extraction plants is usually much less than the critical value for gelation; although the cation content of the tailings pond water is normally well above the critical amount, gelation does not occur immediately and a significant amount of water is released. However, time is not an issue in tailings ponds and hindered settling eventually occurs, leading to the progressive accumulation of sludge through MFT formation. The ultrafines concentration of ∼3 wt% observed in MFT coincides with the critical gelation concentration determined for suspensions of ultrafines in salt solutions with cationic concentrations representative of the chemistry in

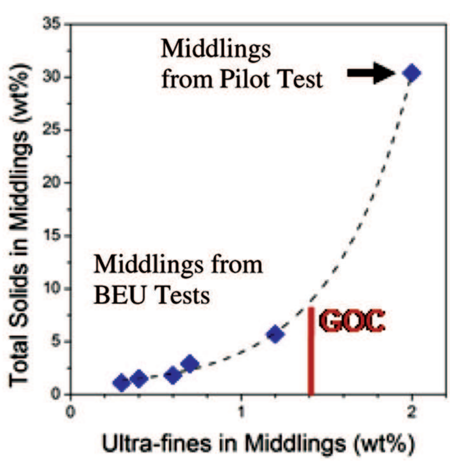

Figure 8. Total solids versus ultrafines contents in middlings from BEU and pilot tests for a number of oil sands. Data from O'Carroll (2000). (color figure available online)

pond water. This observation accounts for 100% of the water-holding capacity of MFT and also explains why virtually no water is released once an MFT gel state has been formed.

4. Conclusions

Ultrafines are predominantly colloidal phyllosilicate clays with dimensions $<0.3\ \mu$m that naturally exist in oil sands and are released into the water phase during processing. In the presence of critical cation concentrations, this oil sands component is capable of forming thixotropic gels at low concentrations. Divalent cations such as calcium and magnesium have an enhanced effect on this process. Even before occurrence of gelation, slurry viscosity or thickening can increase sufficiently to reduce the segregation of coarser solids and prevent bitumen droplet separation. In some cases, adsorbed organic on the surfaces imposes biwettable characteristics on the ultrafines that result in formation of emulsified bitumen droplets that are too small to float easily. Ultrafines deposited into tailings ponds continue to flocculate and settle while entrapping coarser particles within the open structure. Eventually mature fines tailings are formed that always contain the same amount of ultrafines ($\sim$3 wt%) regardless of the total solids content. Ultrafines content therefore represents an important indicator for both bitumen recovery and extent of fine tailings formation. Recent XRD developments for analyzing clay minerals in oil sands may make the determination of this important parameter easier.

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